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Si/SiO_2 INTERFERE STUDIES BY IMMERSION ELLIPSOMETRY

Q. Liu and E.A. Irene
Department of Chemistry
University of North Carolina at Chapel Hill
Chapel Hill, NC 27599-3290

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Q. Liu & E.A. Irene

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CB #3290, Venable Hall
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Q. LIU AND E.A. IRENE
Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, N. C. 27599-3290

Abstract

The mechanisms associated with Si/SiO_2 interface annealing and thermal oxidation conditions were studied by spectroscopic immersion ellipsometry. Essentially, this surface sensitive ellipsometry technique uses liquids that refractive index match with the films, thereby optically removing the films.

With the use of an optical model, it is shown that at high annealing temperatures viscous relaxation dominates, while at low annealing temperatures the suboxide reduction is apparent. It is also shown that with the thickening SiO_2 overlayer, the thickness of the suboxide layer at the interface increases and the average radius of the crystalline silicon protrusions decreases for the three different orientation studied. These results are consistent with the commonly accepted Si oxidation model.

I. Introduction

As semiconductor devices become smaller, ultra-thin films less than 10nm thick find application in integrated circuit technology. Because even a small degree of interfacial microroughness or nonuniformity can alter device performance, it is crucial to control the atomic scale structure. Much work has been done to investigate the Si/SiO_2 interface by different techniques, such as transmission electron microscopy (TEM)[1-2], low-energy electron diffraction (LEED)[3], ellipsometry[4-8], etc., but the details of the interface remain unclear. In the present research, the interface is studied by *spectroscopic immersion ellipsometry*[9,10] (SIE), which is very sensitive to the interface.

Ellipsometry is an optical technique for the characterization of a bare or film covered surface and is based on exploiting the polarization transformation that occurs as a beam of polarized light is reflected from or transmitted through the interface or film[11]. The measured ellipsometric quantity, ρ, is called the complex reflectance ratio and defined as:

$$\rho = \frac{r_p}{r_s} = (\tan\psi)e^{j\Delta} \tag{1}$$

where $\tan\Psi$ is the ratio of the amplitude attenuation, Δ is the total phase shift. r_p and r_s are the Fresnel reflection coefficients for light polarized parallel and perpendicular, respectively, to the plane of incidence.

There are several different ways to study the interface region between film and substrate. One way is by using spectroscopic ellipsometry in air ambient (Fig. 1a). The disadvantage of this method is that an accurate characterization of the ultra-thin interface transition layer is complicated by the inability to discriminate the optical contributions of the relatively thick overlayer and the thin transition layer by the measured ellipsometric parameters. Another way is to remove the overlayer physically

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or chemically and then to probe the interface (Fig. 1b). However, this method could alter the interface region. In order to overcome these problems we have developed the technique of spectroscopic immersion ellipsometry[9,10] (SIE), which uses a transparent liquid ambient that has optical properties very close to the optical properties of the dielectric overlayer thereby eliminating the optical response of the overlayer (Fig. 1c). Hence, this technique "optically" removes the overlayer and thus enhances the sensitivity to the interface properties. The interface sensitivity of Δ is drastically increased using the liquid ambient as is shown in Fig.2 which compares the relative interface sensitivity $\delta\Delta(E) = \Delta_0(E) - \Delta_\infty(E)$ for air and CCl_4 ambient. $\Delta_0(E)$ and $\Delta_\infty(E)$ are calculated without and with an assumed interface layer, respectively[9].

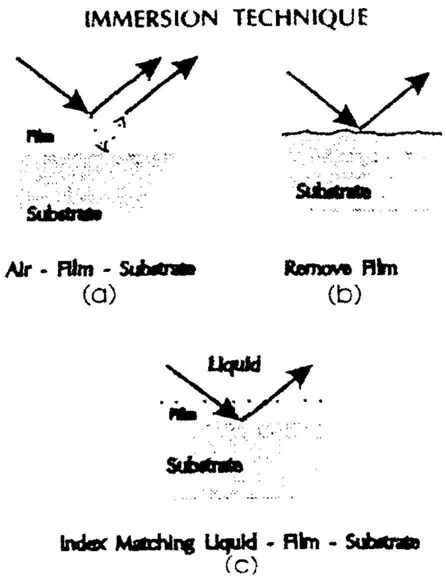

Fig. 1. Immersion technique.

II. Experimental procedures and data analysis

Single-crystal (100), (110), and (111) oriented 2 Ω cm p-type silicon wafers were cleaned using a slightly modified RCA procedure[12] and thermally oxidized in a fused silica tube furnace in clean dry oxygen. A commercially available vertical ellipsometer bench was modified to become a rotating analyzer spectroscopic ellipsometer[13]. A special fused silica immersion cell has been designed for the SIE measurements.

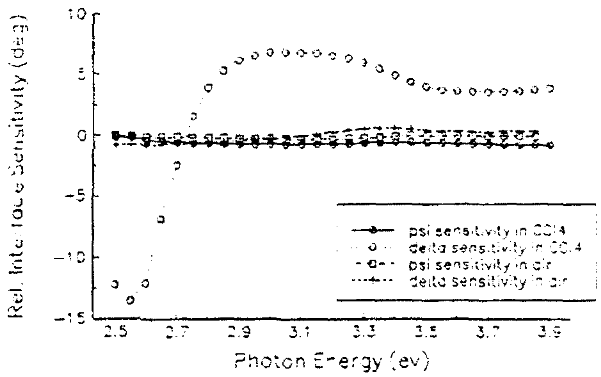

Fig. 2 Interface sensitivity for CCl_4 and air.

Generally, it is difficult to achieve a perfect refractive index match for the liquid ambient and the SiO_2 overlayer over a broad spectral range. Therefore small deviations are accounted for in the analysis. Carbon tetrachloride (CCl_4) is a suitable immersion liquid for index matching to SiO_2 films.

In order to obtain unknown interface parameters, we used a Marquardt and Gauss-Newton nonlinear best fit algorithm which minimizes the value of the error function

$$Q = \sum_{i,j} [(\Delta_{ij}^{cal}(\phi_i, E_j, P) - \Delta_{ij}^{exp})^2 + (\psi_{ij}^{cal}(\phi_i, E_j, P) - \psi_{ij}^{exp})^2] \quad (2)$$

where P is a vector of unknown interface parameters, E_j is the photon energy, ϕ_i is the angle of incidence, and the superscripts cal and exp refer to calculated and experimentally derived values. Δ^{cal} and Ψ^{cal} are the values obtained using the vector P from expanded Fresnel formulas.

In our analysis, the working model for the interface between crystalline Si substrate and amorphous SiO_2 film is shown in Fig. 3. The transition region has a structure with two major components: the "physical" interface and the "chemical" interface. The "physical" interface can be represented by microroughness or protrusions of Si into the oxide. The "chemical" interface consists of a suboxide, SiO_x with $0<x<2$. We describe the crystalline silicon protrusions as hemispheres with an average radius R, which form a hexagonal network with an average distance D between centers. The protrusions and the region between them are covered by a layer of suboxide assumed to be SiO (i.e. x=1) with an average thickness L_{SiO}. An effective interface thickness is given as:

$$L_{inf} = R + L_{SiO} \quad (3)$$

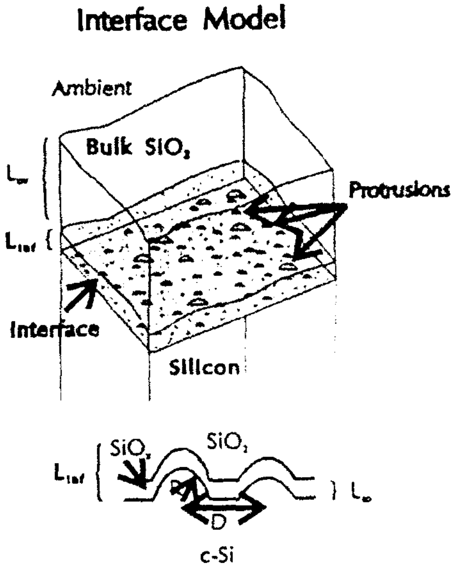

Fig. 2. The interface model.

The Bruggeman effective mediumapproximation (BEMA) was used to calculate the effective dielectric function of the interface[14].

III. Results and discussion

A. SIE study of the mechanism of Si/SiO_2 interface annealing

The evolution of the Si/SiO_2 interface as a function of high temperature annealing (750-1000^{0}C) was investigated by SIE[12]. Fig. 4 shows unmodeled data in terms of an effective relative interface parameter defined as:

$$\delta\Delta_{inf}(T_{an}, t_{AN}) = \Delta^{exp}(T_{an}, t_{an}) - \Delta_0^{exp} - \delta\Delta_{ov}^{cal}(T_{an}, t_{an}), \quad (4)$$

where $\Delta^{exp}(T_{an}, t_{an})$ is the experimental ellipsometric angle Δ at an annealing temperature and time, Δ_0 is the ellipsometric angle for a nonannealed sample and the term $\delta\Delta^{cal}_{ov}(T_{an}, t_{an})$ is the overlayer relaxation correction. Fig. 5 shows modeled data in terms of the interface thickness defined above and which displays the temperature-time dependent shrinkage of the interface with annealing. Distinct modes of behavior are observed for the evolution of the interface. For short annealing times a rapid change in the interface is observed that correlates with the disappearance of protrusions, followed by a slower change that correlates with the disappearance of the suboxide. At high annealing temperatures we believe that viscous relaxation dominates, while at low annealing temperatures the suboxide reduction is apparent.

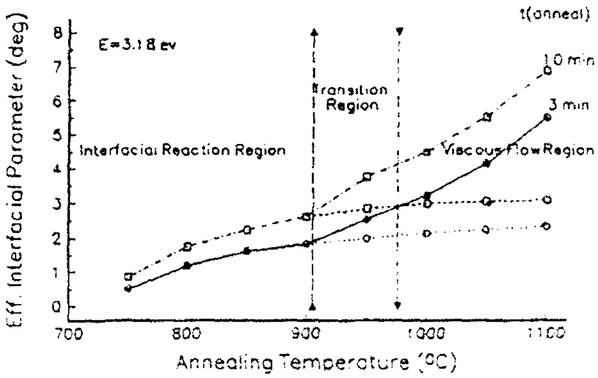

Fig. 4. Annealing temperature dependence of the effective interfacial parameter.

B. SIE study of the interface of Si/SiO_2 for different thermal oxidation conditions

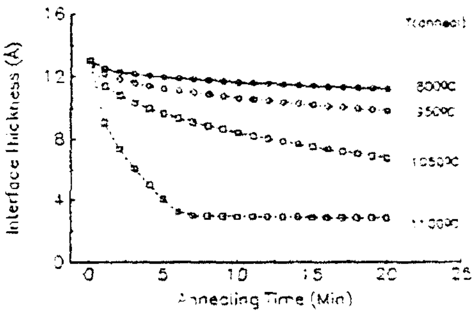

Fig. 5. Annealing time and temperature dependence of interface thickness.

With the use of the above optical model, we found that the thickness of the SiO layer at the interface, L_{SiO}, for all (100), (110), and (111) silicon substrate orientations increased, and the average radius of the crystalline silicon protrusion, R, decreased with the thickening of the SiO_2 overlayer as shown in Fig. 6 and 7. These results are consistent with the well accepted linear-parabolic, LP, Si oxidation model[15] which yields an accurate representation of the growth of SiO_2 on Si over a wide range of thickness, temperature and oxidant partial pressures[16]. According to the LP model, the relationship between film thickness, L, and oxidation time, t, is[16]:

$$t - t_0 = \frac{(L - L_0)}{k_l} + \frac{(L^2 - L_0^2)}{k_p} \qquad (5)$$

where the linear, k_l, and parabolic, k_p, rate constants are given as:

$$nk_l = \frac{C_1 k}{\Omega}, \quad k_p = \frac{2DC_1}{\Omega} \qquad (6)$$

where $n = 2.3 \times 10^{22}$ cm^{-3}, k is the reaction rate constant, D the oxidant diffusion coefficient, the subscript 0 denotes the initial values, and C_1 is the concentration of oxidant at the Si surface.

For long oxidation times, the equation (5) reduces to: $t \approx L^2/k_p$. This is termed the parabolic growth law and implies that oxide growth is diffusion controlled. In other words, as the oxide layer gets thicker, the oxidizing species must diffuse through a larger distance to arrive at the Si/SiO_2 interface. The reaction thus becomes limited by the rate at which the oxidizing species diffuse through the oxide. It was shown that at elevated temperatures and with an oxygen deficiency, SiO_2 decomposition takes place:

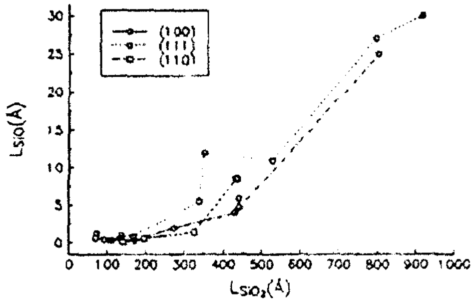

Fig. 6 SiO_2 film thickness dependence of the thickness of L_{SiO} at the interface.

$$SiO_2 + Si \rightarrow 2SiO$$

The oxide decomposition reaction is initiated at active defect sites already present at the Si/SiO_2 interface[17]. In our model the Si protrusions may be considered as defects that could cause the above decomposition, since these sites are thermodynamically active due to the smaller radius of curvature. This is consistent with our results in Figs. 6 and 7 which shows that with the thickening of the SiO_2, the thickness of SiO layer, L_{SiO}, at the interface increases and the average radius of the crystalline protrusions, R, decreases.

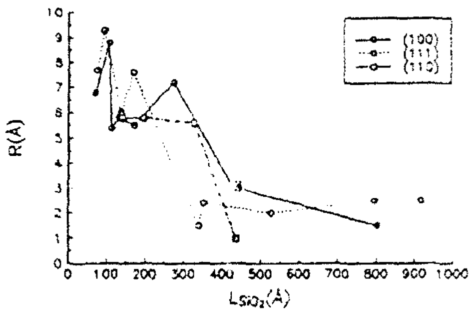

Fig. 7. SiO_2 thickness dependence of the protrusions of radius R at the interface.

IV. Conclusions

An enhanced interface ellipsometry technique, SIE, was applied to study the mechanism of Si/SiO_2 interface annealing and thermal oxidation. By using an optical model, it was shown that different mechanisms dominated at high and low annealing temperature. It was also shown that the thickness of SiO layer at the interface increases and the average radius R of the crystalline silicon protrusions decreases with the thickening SiO_2 overlayer and no orientation effect was observed.

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